Journal of The Electrochemical Society, **152** (12) A2281-A2284 (2005)
0013-4651/2005/152(12)/A2281/4/$7.00 © The Electrochemical Society, Inc.

Synthesis and Characterization of Single-Ion Graft Copolymer Electrolytes

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A microphase-separating single-ion conductor, poly[(oxyethylene)$_9$ methacrylate-*ran*-lithium methacrylate]-*graft*-poly(dimethyl siloxane), P(OEM-*r*-LiMA)-*g*-PDMS, was prepared by lithiating a precursor polymer synthesized by free radical methods using commercially available macromonomers. This material possessed a low conductivity, stemming from high ion-pairing interactions that severely restricted the number of charge carriers available for conduction. Subsequent conversion of the LiMA units via the addition of BF_3, a Lewis acid, resulted in a 2 orders-of-magnitude rise in conductivity, a gain that could be attributed to a large increase in the number of mobile cations. By blending this material with uncharged POEM-*g*-PDMS, the room-temperature conductivity was optimized to 7×10^{-6} S/cm. With a lithium transference number of unity, these materials exhibit higher dc-measured conductivities at elevated currents than their salt-doped counterparts and are electrochemically stable to ~4.5 V.
[DOI: 10.1149/1.2073089]

Manuscript submitted May 5, 2005; revised manuscript received July 18, 2005. Available electronically October 13, 2005.

Polarization in batteries adversely impacts performance, especially at high currents. In salt-doped systems, a major component of this polarization arises from the presence of mobile anions, which allows for the formation of concentration gradients in the cation population.[1-4] The accompanying ohmic potential (iR) drop reduces the capacity of the overall battery by narrowing the voltage window seen by the electrodes. In addition, depletion regions are created deep within the composite cathode on discharge.[4] These problems are expected to be mitigated when the electrolyte's lithium transference number is unity.[4]

Previous attempts to produce single-ion conductors have met with mixed success. In 1985, Tsuchida et al. showed that poly(lithium methacrylate-*ran*-oligooxyethylene methacrylate) had a room-temperature conductivity on the order of 2×10^{-7} S/cm.[5] Ion-pairing between the bound anion and the lithium cation rendered the charge carriers largely immobile. One year before, Bannister et al. obtained a room-temperature conductivity of $\sim 1 \times 10^{-9}$ S/cm from a blend of poly(lithium sulfoethyl methacrylate) and polyethylene oxide (PEO);[6] here, lithium motion was hindered not by ion interactions but by the crystallinity of PEO. Subsequent research on blends and copolymers containing sulfonate[7-9] or fluorinated sulfonate[8,10] anions produced electrolytes with room-temperature conductivities as high as $\sim 1 \times 10^{-5}$ S/cm.[8] A separate strategy employed particles as immobile counterions. Low-molecular-weight polymer/aluminate nanocomposite[11-14] and silicate/solvent[15,16] electrolytes showed conductivities on the order of 1×10^{-5} and 1×10^{-4} S/cm, respectively. Still other approaches to obtaining high-t_{Li^+} conductors include use of a bulky oligo/polymeric counterion[17-19] or creation of anion trap sites[20,21] within the electrolyte. While the conductivities of these systems are higher, the lithium transference number falls short of unity.

In this study, we seek to produce a high-conductivity, mechanically stable, single-ion conducting polymer that can be synthesized by straightforward methods. Microphase-separating block copolymer electrolytes (BCEs) are attractive due to the unusual combination of mechanical and electrical properties this class of materials exhibits.[22-32] An example of such a material previously developed in this laboratory is the microphase-separating graft copolymer electrolyte (GCE) comprising a backbone of poly[(oxyethylene)$_9$ methacrylate] (POEM) and long side chains of poly(dimethyl siloxane) (PDMS). The material can be prepared by simple free-radical polymerization and possesses a room-temperature conductivity near 10^{-5} S/cm when doped with lithium triflate.[26] In the present study we demonstrate that with a slight modification to the synthesis, POEM-*g*-PDMS can be tailored to form a single-ion conductor with room-temperature conductivity comparable to salt-doped systems through the incorporation of lithium methacrylate (LiMA) and subsequent complexation with BF_3. With a transference number of unity, at high current densities these electrolytes exhibit higher dc-measured conductivity than their salt-doped counterparts.

Experimental

Random copolymers of poly(dimethyl siloxane) monomethacrylate macromonomer (PDMSMA, Aldrich, $M_n \approx 10$ kg/mol), poly(ethylene glycol) methyl ether methacrylate, herein called (oxyethylene)$_9$ methacrylate (OEM, Aldrich, $M_n \approx 475$ g/mol), and methacrylic acid (MAA, Aldrich) were prepared by free radical synthesis (Fig. 1). Monomer amounts of 2.3, 10, and 1.9 mL, respectively, were added to 100 mL of ethyl acetate in a flask. The target composition for this material was a 1:1 molar ratio of OEM to MAA and a PDMS weight fraction of 15%. 2,2′-azobisisobutyronitrile (AIBN, Aldrich) initiator was then added at a monomer to initiator ratio of 250:1. The resulting mixture was purged with argon for 30 min, sealed, heated to 72°C, and stirred for 48 h. After polymerization, the material was precipitated in petroleum ether, redissolved, and precipitated four additional times, then washed with deionized water. The recovered graft copolymer product, P(OEM-*r*-MAA)-*g*-PDMS, was then dried for a week at 100°C under vacuum. From ^{1}H NMR the MAA:OEM molar ratio was determined to be 1:1, while the PDMS weight fraction was 11%, corresponding to an overall weight ratio of 75:14:11 (OEM:MAA:PDMS) and an EO:Li ratio of 8:1.

After drying, the polymer was dissolved in anhydrous tetrahydrofuran (THF, Aldrich) and methanol (40:60 ratio, Aldrich) and lithiated via the addition of a stoichiometric amount of lithium methoxide (1:1 molar with respect to the carboxylate, Aldrich). The solution was allowed to stir overnight inside a glove box held below 2 ppm moisture before the solvents were evaporated off in an inert environment. Approximately half of the lithiated material was redried at 100°C under vacuum for several days. A stoichiometric amount of BF_3 (Aldrich) then was added to a solution of the dried polymer and anhydrous THF/methanol, and after 12 h of stirring, the product was cast on a crystallization dish and dried. Fourier transform infrared (FTIR) results shown in Fig. 2 suggest complete conversion of the anion;[25,33] upon the addition of BF_3, the carboxylate C–O vibration found at $\sim 1600\ \mathrm{cm}^{-1}$ shifted outward to $\sim 1720\ \mathrm{cm}^{-1}$.

A second graft copolymer (POEM-*g*-PDMS) with roughly equivalent PDMS content (13%) was also prepared by free radical methods. This copolymer was blended with the first material in order to optimize the overall lithium concentration in the electrolyte

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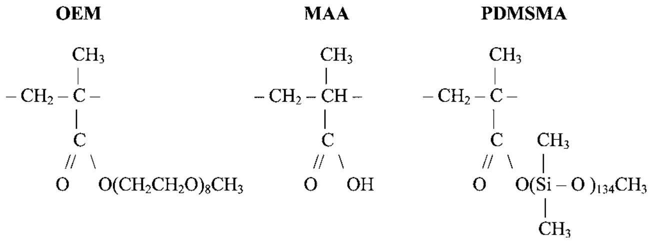

Figure 1. The structure of the repeat units present in the copolymer precursor. Methacrylic acid (MAA) was subsequently lithiated and complexed with BF_3.

without changing substantially the volume fraction of the ion-conducting domains. To verify that such blends performed comparably to their single-component counterparts, a second single-ion GCE (1:16 EO:Li ratio and a PDMS fraction of ~29%) was synthesized using the procedure described above, although with *tert*-butyl methacrylate (tBMA, Aldrich) in place of methacrylic acid. Here, the material was hydrolyzed at 100°C in a solution of toluene and *p*-toluenesulfonic acid (5 mol % with respect to the tBMA, Aldrich) before lithiation.[34] Finally, an electrolyte of POEM-*g*-PDMS (70:30) doped to 20:1 EO:Li with lithium triflate ($LiCF_3SO_3$, Aldrich) was prepared as described previously.[26]

The electrochemical stability of the material was assessed by cyclic voltammetry (CV). The electrolyte was pressed between an oversized counter electrode of lithium and an 0.5 cm^2 working electrode of platinum to a film thickness of approximately 200 μm. The potential was scanned from +2.5 to + 5.5 V at a sweep rate of 10 mV s^{-1} using a Solartron 1286 electrochemical interface (Solartron Analytical, Houston, TX) controlled by a personal computer running CorrWare (Scribner Associates, Inc., Southern Pines, NC).

The lithium transference number was measured in lithium symmetric cells fitted with electrolyte specimens measuring 300–500 μm in thickness. In such cells the only electrode reactions involve contributions from lithium ions; anions are rendered faradaically inactive. Following the application of a stepped potential, the initial current (I_o) reflects contributions from both the cation and anion, whereas the long-term, steady-state value (I_{ss}) is the result of lithium ion motion alone. Accordingly, the transference number can be taken to be I_{ss}/I_o. This simplified method does not take into account the concentration dependence of the lithium diffusion coefficient,[35] nor does it correct for any changes in the iR drop across electrode surface films due to a variation in current or film thickness during the course of the test.[36] However, if the transference number is measured to be unity these sources of error are absent. The observation that the current response is invariant with time is evidence that no ion concentration gradients exist in the electrolyte.

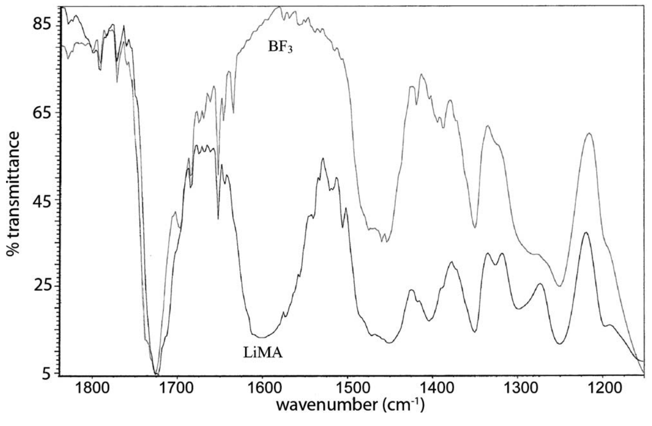

Figure 2. FTIR spectra comparing precursor P(OEM-*r*-LiMA)-*g*-PDMS to the same material after the addition of BF_3. The shifting of the peak at ~1600 cm^{-1} associated with the carboxylate C–O bond is evidence of BF_3 complexation.

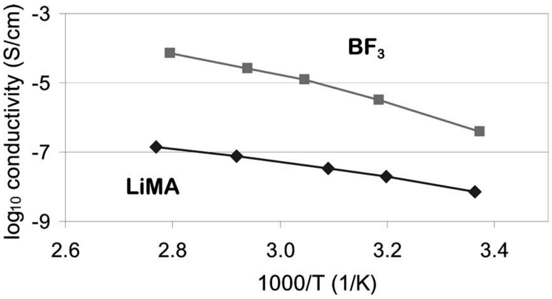

Figure 3. Temperature dependence of electrical conductivity of the 1:8 single-ion GCE systems, with and without BF_3.

AC conductivity was obtained by impedance spectroscopy using a waveform generator/response analyzer (Solartron model 1260 frequency response analyzer, Solartron Analytical, Houston, TX) controlled by a personal computer running commercially available software (Z60, Scribner Associates, Inc., Southern Pines, NC). The test fixture consisted of two blocking electrodes made of stainless steel and attached to a micrometer which measured the electrode separation and, hence, the thickness of the polymer specimen. All tests were performed in an atmosphere of flowing argon gas.

Lithium symmetric cells were used in dc conductivity measurements. A constant potential was applied to cells fitted with the various electrolytes; the measured current yielded the resistance (and thus the dc conductivity) via Ohm's law. Unlike ac impedance using blocking electrodes, dc conductivity measurements take into account contributions from the charge transfer and interfacial film resistance present at the lithium electrodes. The tests are influenced both by the transference number and ac-measured conductivity values of the material and thus differ from actual cell cycling only by the absence of effects stemming from the intercalating cathode.

Results and Discussion

Figure 3 shows the variation of conductivity with temperature for P(OEM-*r*-LiMA)-*g*-PDMS with a Li:EO ratio of 1:8, as well as for the same material incorporating BF_3. For the carboxylate material, the conductivity was low ($<10^{-8}$ S/cm), indicative of ion-pairing observed previously in studies on electrolytes of similar chemical structure.[25,37] Complexing of COO^- with BF_3 led to a 2 orders-of-magnitude rise in conductivity, consistent with the gains seen by Florjanczyk et al.[33] and in our previous work.[25]

To optimize the conductivity of the electrolyte, the Li:EO ratio of 1:8 in this system was diluted through the addition of uncharged POEM-*g*-PDMS having 13 wt % PDMS. The conductivity of such a blend with a Li:EO ratio of 1:16 was measured to be virtually identical to that of the nonblended P(OEM-*r*-LiMA)-*g*-PDMS system synthesized with the same Li:EO ratio. As anticipated, blending proved to be an acceptable method for adjusting the lithium concentration.

Isotherms taken at room temperature and 90°C (Fig. 4) show that the lithium concentration at which conductivity goes through a maximum is dependent upon temperature. Qualitatively, the peak displayed in the isotherms arises from two competing trends. Diluting the single-ion GCE diminishes the concentration of charge carriers while at the same time increasing ion mobility, both by reducing ion clustering and ion-chain coordination and by freeing up sites into which the ions can diffuse.[38-40] Raising the temperature increases the mobility of the ions by providing the energy required to overcome the activation barrier to diffusion; at high temperatures, concentrated electrolytes are favored as the impediments to ion motion become less significant. This interpretation can be validated by

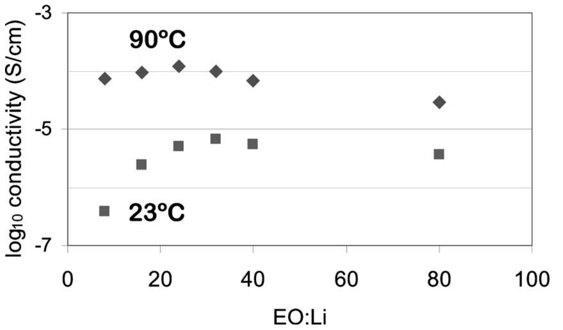

Figure 4. Isothermal variation of electrical conductivity with ethylene oxide:lithium ratio at room temperature (~23°C) and 90°C for the BF_3-incorporated single-ion GCE systems.

parametrically fitting the conductivity data to the Vogel–Tammann–Fulcher (VTF) equation, an empirical relationship loosely based on combining the Nernst–Einstein equation for ion diffusion with the Stokes–Einstein equation, which relates charge-carrier diffusion coefficients to matrix viscosity[41,42]

$$\sigma = AT^{1/2} \exp[- E_a/k(T - T_o)] \qquad [1]$$

The pre-exponential term A relates directly to the number of charge carriers in the system, T is the absolute temperature, and T_o is a reference temperature associated with the glass transition temperature, T_g, of the conducting polymer host. T_o usually falls 25–50° below T_g. The activation energy E_a scales inversely with the ease of motion of the charge carriers.

Table I lists the VTF parameters for the single-ion GCEs and their blends as measured in this study. Differential scanning calorimetry (DSC) measurements of these systems (Table I) show a decrease in T_g upon dilution, and in general the T_o values seem to follow the same trend (assuming that the 1:8 BF_3 electrolyte is an outlier). For the carboxylate material, A is found to be extremely low; high ion-pairing interactions effectively immobilize most of the lithium cations. Incorporation of BF_3 facilitates lithium-ion dissociation, boosting the value of A by several orders of magnitude. Dilution through the addition of POEM-*g*-PDMS lowers the number of charge carriers but also reduces the activation energy required for ion motion. As speculated, the maximum in conductivity seen in Fig. 4 appears at the concentration that yields the optimum product of ion mobility and charge-carrier population. At elevated temperatures, the added thermal energy somewhat mitigates the effects of E_a, and the peak conductivity is obtained for materials with higher Li^+ concentrations. Of note, the maximum room-temperature conductivity, 7×10^{-6} S/cm, for Li:EO 1:32 is close to that obtained for a GCE-doped 20:1 EO:Li with lithium triflate ($\sigma \sim 8 \times 10^{-6}$ S/cm).

In transference number measurements on single-ion GCE blends, following the application of a stepped dc potential across a lithium symmetric cell, the current jumped, remained constant, and showed no signs of polarization over a period of 1 h. Hence the transference number of Li^+ in these systems, t_{Li^+}, is judged to be ~1. In addition, these materials exhibited no evidence of electrochemical breakdown at voltages as high as 4.5 V.

Table I. Optimized VTF parameters obtained from fitting the measured values of electrical conductivity data and glass transition temperatures from DSC of the single-ion GCEs.

	A (S $K^{0.5}$ cm^{-1})	E_a (eV)	T_o (K)	T_g (K)
Li 1:8	1.46×10^{-4}	0.058	215.2	211
BF_3 1:8	4.80	0.112	202.2	249.7
BF_3 1:16	4.4×10^{-1}	0.073	208.0	229.5
BF_3 1:24	2.4×10^{-1}	0.066	202.2	222.5
BF_3 1:32	1.0×10^{-1}	0.057	201.8	217.5

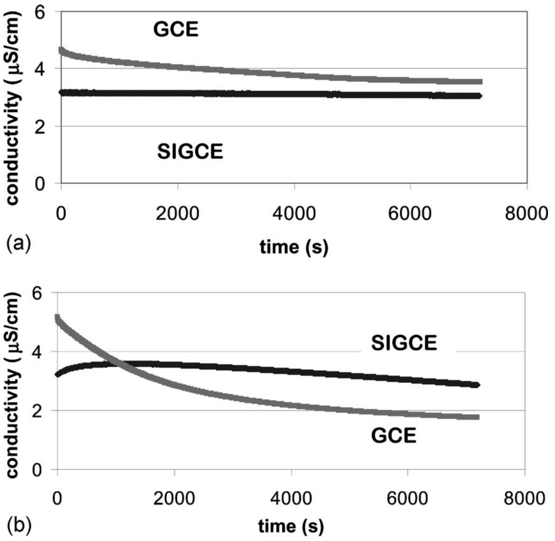

Figure 5. Comparison of the variation in dc-measured conductivity with time between lithium-triflate-doped POEM-*g*-PDMS (70:30) and 1:24 BF_3-incorporated single-ion GCE (SIGCE 1:24). Measurements taken at room temperature in a lithium symmetric cell: (a) 0.01 V (~1.25 μA/cm²) and (b) 0.25 V (~32 μA/cm²). Note that the room-temperature, ac-measured conductivity values of these materials are 7.8 and 4.91×10^{-6} S/cm, respectively.

Figure 5 compares dc conductivity measurements for lithium-triflate-doped POEM-*g*-PDMS (70:30) and a 1:24 blend incorporating BF_3. At low currents the dc-measured conductivity is greater for the lithium triflate system due to its higher ac-measured conductivity ($\sigma = 7.8 \times 10^{-6}$ S/cm for the salt-doped material vs 4.91×10^{-6} S/cm for single-ion conductor, both measured at room temperature). In time, however, the evolution of concentration gradients in lithium triflate reduces the performance advantage of the GCE over the single-ion electrolyte, even at currents as low as ~1.25 μA/cm². At higher voltages, the salt-doped system's performance becomes increasingly limited by polarization. At a current density of ~32 μA/cm², the single-ion GCE outperforms the salt-doped electrolyte, suggesting that the former system should support higher currents in batteries where transport within the electrolyte is the rate-limiting step.

Conclusions

In this work, ion-pairing interactions are overcome in microphase-separating polymer single ion-conductors by use of a large anionic moiety that readily delocalizes charge, thus achieving high conductivities while still maintaining a lithium-ion transference number of ~1. The single-ion GCEs investigated in this work can be made by simple, scalable techniques, display rubbery mechanical behavior, and are easily processed by solvent-casting methods. DC conductivity measurements suggest that such systems may outperform their salt-doped counterparts at high current densities.

Acknowledgments

This project has been sponsored by the Office of Naval Research under contracts N00014-99-1-0561, N00014-99-1-0565, N00014-02-1-0226, and N00014-05-0056 and in part by the MIT MRSEC Program of the National Science Foundation under award DMR-0213282.

Massachusetts Institute of Technology assisted in meeting the publication costs of this article.

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